Unoccupied electronic structure of single-crystal La_2CuO_4

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Single crystals of lanthanum cuprate have been studied using k-resolved inverse photoemission. The predicted dispersion of the Cu $3d$–O $2p$-derived band through the Fermi level is not observed and this may influence models for high-temperature superconductivity based on band-structure calculations. In addition, resonant inverse photoemission of the lanthanum-derived features is also observed at the plasmon frequencies.

The discovery of high-T_c superconductivity[1] in the doped lanthanum cuprates $La_{2-x}B_xCuO_4$ and the subsequent development of a wide range of copper-oxide-based superconductors has led to a diverse number of theoretical ideas attempting to understand the properties of these compounds.[2–4] Early models based on the electron-phonon interaction[4] depended strongly on the predictions of electronic band-structure calculations.[5–8] Photoemission studies have been highly successful in determining band structures of a wide range of materials and should in principle be able to test the validity of such calculations for these new compounds. However, initial experiments[9–11] found a discrepancy between theory and experiment in the absolute binding energies of the different valence features. The complementary technique inverse photoemission spectroscopy (IPES), which probes the empty states, also produced discrepancies with calculation. In particular, both experimental methods find a very low density of states at the Fermi level. A more rigorous test of the band-structure calculations is provided by angle-resolved studies of single crystals. As yet photoemission studies of such crystals have not provided clear evidence of dispersing bands near the Fermi level,[12] although a recent study of the new high-T_c material appears to provide more compelling evidence.[13] However, the large number of occupied bands in these materials tends to complicate the interpretation of features observed in the photoemission spectra. Above the Fermi level the number of bands is reduced and as such any dispersing unoccupied bands probed by IPES should be easier to identify. In this paper, we present the first k-resolved inverse photoemission spectroscopy (KRIPES) results from a single crystal of La_2CuO_4, the high-T_c superconductor parent compound.

Lanthanum cuprate La_2CuO_4 has been extensively studied[14–17] in order to gain insight into the properties of the doped materials. Structural studies[15] have shown the room-temperature form to be an orthorhombic distortion of the tetragonal K_2NiF_4 structure. The orthorhombic-to-tetragonal phase transition temperature (T_0) depends critically on the oxygen content:[16] for La_2CuO_{4-x}, $T_0=506$ K with $x=0.0$ and $T_0=536$ K with $x=0.03$. Neutron-diffraction studies[17] have found that oxygen-deficient samples are antiferromagnetic with a Néel temperature which also depends on the stoichiometry. La_2CuO_4 represents a tractable problem for band-structure methods and calculations have been carried out for both the tetragonal[5,6] and orthorhombic[7] phases and, more recently,[8] the possibility of antiferromagnetic order has been considered.

Calculations predict two-dimensional bands crossing the Fermi level which represent antibonding Cu $3d(x^2-y^2)$ and O $2p(x,y)$ orbitals restricted to the copper-oxygen planes normal to the c direction. KRIPES studies of the $La_2CuO_4(001)$ face should be able to observe such dispersing bands in the Γ-X direction of the tetragonal structure. The observation of a Cu $3d$–O $2p$ peak in earlier IPES studies[18] of polycrystalline samples of $YBa_2Cu_3O_7$ suggests that the cross section is sufficient at the energies employed.

The single crystals of La_2CuO_4 were grown by the flux method and were large ($\simeq 5\times5\times1$ mm^3) with high-quality reflecting surfaces perpendicular to the c axis. Two crystals were studied, one hand polished with diamond paste to a 0.25-μm finish and the other as grown but etched with dilute acetic acid to relieve surface strain. The results are essentially the same for both samples.

The experiments were carried out in a surface science chamber equipped with standard low-energy electron diffraction (LEED) and Auger electron spectroscopy for monitoring the surface condition. As has been described in detail elsewhere,[19] the photons emitted in the inverse photoemission process are detected with a grating spectrograph operating in the range 10–40 eV. For low-incident electron-beam energies, the overall resolution is determined by the energy spread of the electron source, typically 0.3 eV. At higher energies (e.g., 30 eV, the resolution is dominated by the wavelength resolution of the spectrograph and is of the order of 0.75 eV.

The samples were subjected to a cautious regimen of annealing and argon ion bombardment. As is described in more detail elsewhere,[20] a good 1×1 pattern was established over a large portion of the crystal surface after 40-min total annealing time. The 1×1 surface could be destroyed by argon ion bombardment and restored by annealing. Following 90-min cumulative annealing an irreversible transition took place from a 1×1 to a 1×8 LEED pattern. After prolonged annealing, charging was observed in room-temperature spectra. In such cases, raising the sample temperature eliminated the problem.

In Fig. 1 we show normal incidence spectra from the ordered (1×1) $La_2CuO_4(001)$ surface both at room temperature and 850 K. In both spectra the incident beam energy is 32.85 eV with respect to the Fermi level. In agreement with our earlier studies[18] of polycrystalline samples, the room-temperature spectrum shows a strong peak at 9 eV but no evidence of any structure at or near the Fermi level. An intense peak at 6 eV, which is associated with the La $5d$ level, shows a strong resonance in this energy range as do the $4f$ levels at higher energies. No such intensity increase is observed in the Fermi energy region. The peak positions may be compared with band-structure calculations[5-8] where the La $5d$ bands are found to peak at approximately 3 eV above the Fermi level and the La $4f$ levels at 3.5–4 eV above E_F. The difference may partially reflect the fact that the inverse photoemission process represents an excitation spectrum.

There is also a difference in the peak positions between the room-temperature and 850-K spectra. This may be related to the structural change or possible charging effects. However, the two peaks shift by differing amounts producing a real change in the relative positions of the La $5d$ and $4f$ levels. No other differences are observed on changing the temperature; the same LEED pattern is seen at all temperatures and is consistent with the tetragonal phase. In the following discussion, the tetragonal phase will be assumed for simplicity.

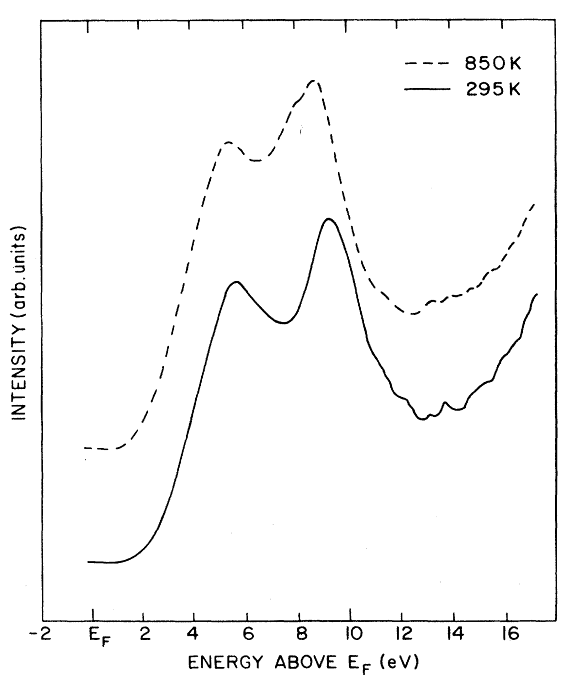

FIG. 1. Inverse photoemission spectra recorded from La_2CuO_4 as a function of temperature. The specimen temperature for the two spectra is indicated. The incident electron-beam energy is 32.85 eV with respect to the Fermi level.

Figure 2 shows a typical range of spectra recorded for different angles of incidence of the electron beam with fixed incident energy 24.35 eV above the Fermi level. There is only very weak structure immediately above E_F and no discernible Fermi edge. The broad feature centered at 1.7 eV above E_F is frequently observed; this is probably due to contamination and can be reduced by flashing the sample. The same result was obtained independent of incident energy or crystallographic direction. Significantly, the same experiments above the Néel and orthorhombic-to-tetragonal transition temperatures showed no peak dispersion nor intensity at the Fermi level. Even if a Peierls-type distortion or antiferromagnetic order leading to a semiconducting gap is considered, dispersing bands should still be observable above the Fermi level at room temperature. Perturbation due to relaxation effects should be considerably less for the Cu $3d$–O $2p$ bands since they are thought to be essentially free electronlike as compared to the more localized La levels.

Examination of Figs. 1 and 2 shows that the relative intensity of the La $5d$ and $4f$ peaks changes as a function of photon energy. This is demonstrated more clearly in Fig. 3 where we show the normalized intensity of these two features as a function of photon energy. The $5d$ level clearly shows an intensity maximum centered at $h\nu=29\pm1$ eV with a full width at half maximum

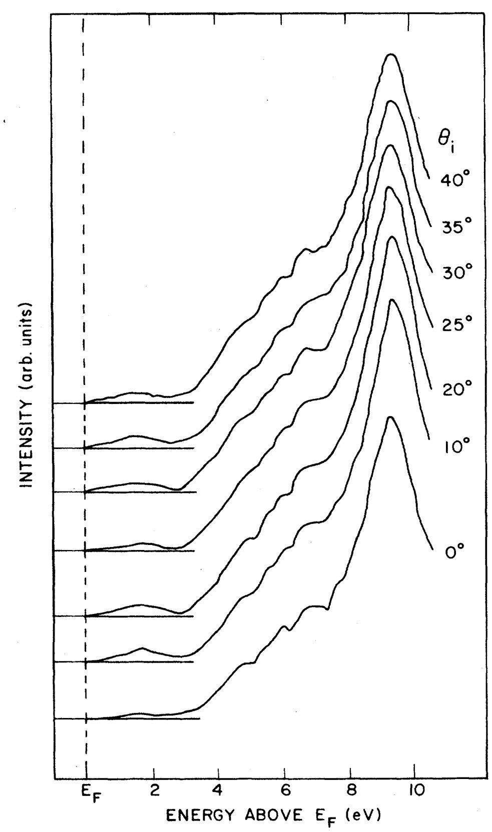

FIG. 2. Inverse photoemission spectra recorded from room temperature La_2CuO_4 as a function of the angle of incidence. The energy of the incident beam is 24.35 eV with respect to the Fermi level.

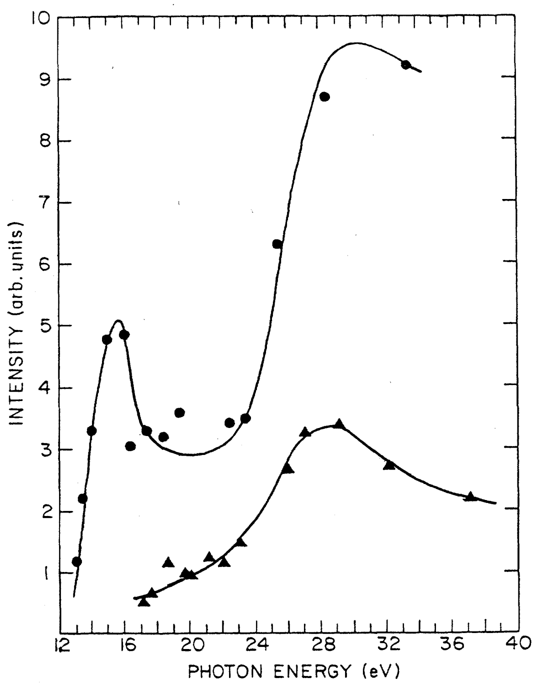

FIG. 3. Intensity of the lanthanum $5d$ level (▲) and $4f$ (○) as a function of photon energy.

(FWHM) of 8 eV. The La $4f$ also displays an intensity increase in this region and further shows narrow intensity maximum at $h\nu = 15$ eV. Recent work[21] has shown that resonant enhancement can occur at the bulk-plasmon energy. Broad plasmon features are observed at approximately 14 and 29 eV below the La $4d$ levels in x-ray photoemission spectroscopy (XPS) data taken from both polycrystalline and single-crystal La_2CuO_4 samples.[22] The observed resonance of the $5d$ level appears at the higher plasmon energy, the intensity increasing by a factor of approximately 4 and this results in a significant modification of the spectral shape. The intensity of the $4f$ level also appears to increase at the lower plasmon energy. Resonant coupling of this type appears to indicate non-free-electron-like behavior and, indeed, materials such as Al do not show such a phenomenon.[20] No obvious increase in intensity is observed at or near the Fermi level. The resonance behavior appears to be insensitive to the surface order and is observed for both the (1×1) and (1×8) surfaces (at room temperature and 850 K) as well as for the disordered surface.

It is also possible that the intensity increase may be associated with the excitation of the La $5p$ core level to the unoccupied $5d$ levels leading to resonant behavior. One would anticipate that threshold for such an excitation would be less than or equal to the sum of the measured binding energy of the $5p$ level and the energy of the $5d$ level above E_F. This sum would be 23 eV, i.e., less than the 29 eV in the present study. However, such a resonance effect was not observed in pure Lanthanum metal, although[23] fluorescence resulting from the radiative decay of the $5p$ core hole was observed. A decay of that type favors valence $5d$ to $5p$ core-level transitions. The complete absence of fluorescence in the present material suggests that the La $5d$ level is no longer occupied in the perovskite structure.

In summary, while we are able to identify the different features in the unoccupied density of states, the low intensity at the Fermi level, and the complete lack of any observed band dispersion means that a direct comparison with band-structure calculations is not successful. It is not clear whether this is an artifact of the surface region or whether it indicates a fundamental problem with the applicability of band theory to this material.

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